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VULCANIZATION AND STRESS-STRAIN BEHAVIOR OF SOL, GEL, AND TOTAL RUBBER HYDROCARBON

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ABSTRACT

Sol, gel, and total rubber hydrocarbon, prepared by a method previously described in this journal, were each compounded and vulcanized under three sets of conditions. In one case, tetramethylthiuram disulphide, a rapid accelerator of vulcanization was used. In another, triphenylguanidine, a slow accelerator was used, and in the third case the rubbers were vulcanized at room temperature by the Peachey process. The stress-strain properties of the vulcanized rubbers were determined and found to be similar for each type of cure. Vulcanized rubbers prepared from the insoluble rubber hydrocarbon were less extensible, and those prepared from the soluble rubber hydrocarbon more extensible than those prepared from the total rubber hydrocarbon.

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INTRODUCTION

The existence and significance of a soluble and an insoluble fraction in rubber hydrocarbon and the proportions in which they occur have long been the subject of conflicting reports, which have been summarized in a previous paper.[1] They were the basis of a two-phase theory of rubber structure proposed by Fessenden.[2] The history of the subject need not be reviewed here. Early knowledge of it was summarized by Engler and Herbst [3] in 1887 and an excellent historical treatment has been given by Whitby.[4]

The differing solubilities and other characteristics of the two fractions suggested a study of their behavior when vulcanized. A sufficient quantity of rubber hydrocarbon for the purpose was purified and separated into the soluble and insoluble fractions by extraction with ethyl ether, suitable compounds of each were mixed and vulcanized, and comparative tests made.

II. PREPARATION OF FRACTIONS

Purified rubber hydrocarbon was obtained from the latex of *Hevea brasiliensis* by a method previously described in this journal.[5] The main purpose of the method of purification was to separate the

[1] BS J.Research **10,** 479(1933);RP544.
[2] Sci. **20,**52(1892).
[3] Ladenburg's Handwörterbuch der Chem. **5,**479(1887).
[4] Colwyn Medal Essay. Trans. Inst. Rubber Ind. **6,**42(1930–31).
[5] See footnote 1.

fractions as sharply as possible while maintaining the structure of the rubber hydrocarbon as it exists in the latex. The purified hydrocarbon was separated into two fractions by thorough, continuous extraction with ethyl ether for several days. A stream of nitrogen was used to displace oxygen in the ether and a little phenyl-β-naphthylamine, a commercial antioxidant, was added to the ether from time to time during the separation of the fractions. The soluble fraction constitutes approximately 75 percent of the total rubber hydrocarbon, and the insoluble or gel fraction, 25 percent. The separated rubber fractions were desolvated by acetone, and the residual acetone and ether were removed from the rubber in vacuo. A little of the phenyl-β-naphthylamine which was in the ether during extraction remained in the rubber hydrocarbon, and, after the removal of the acetone and ether, an additional 1 percent of it was milled into each fraction. Whenever it was necessary to preserve the fractions, they were kept in a desiccator filled with nitrogen.

III. VULCANIZATION OF THE FRACTIONS AND RESULTS OF TESTS

Before the fractions of rubber hydrocarbon were vulcanized, the possible effect of ethyl ether, not completely removed, was determined with pale crepe. Solvents have a softening action and change the physical properties of vulcanized compounds. A sample of pale crepe was allowed to remain in contact with ether until the soluble fraction formed a very viscous solution. The ether was then removed in vacuo, and the residual rubber and a sample of the original pale crepe were compounded as follows:

Ingredients	Parts by weight
Pale crepe	100
Sulphur	3
Zinc oxide	5
Diphenylguanidine	1
Stearic acid	0.75

Samples were vulcanized simultaneously for 20 and also for 30 minutes at 142° C. For each cure, the stress-strain properties of compounds representing rubber treated and untreated with ether were alike to 600 percent elongation. There were slight but negligible differences at higher elongations. It was evident that, for the purposes of this work, the use of ether in separating the fractions did not cause differences in tensile characteristics such as are indicated in figure 1.

Preliminary work on the behavior of the fractions when vulcanized was carried out with a compound containing tetramethylthiuram disulphide, a rapid accelerator of vulcanization. A small quantity of compound containing each fraction was mixed on a laboratory mill and vulcanized in the form of rings. Tests of the vulcanized soluble fraction indicated a modulus, at 500 percent elongation, of 500 lb/in.^{2}. The modulus of the vulcanized insoluble fraction at the same elongation was 250 lb/in.^{2}. The insoluble (gel) fraction produced a much stiffer compound than the soluble (sol) fraction.

It appeared desirable to use a slow accelerator of vulcanization to accentuate any differences in the fractions through the greater diver-

gences of the stress-strain properties. Triphenylguanidine was chosen, and the following compound was used:

Ingredients	Parts by weight
Rubber	100
Sulphur	3
Zinc oxide	5
Stearic acid	1
Triphenylguanidine	2
Phenyl-β-naphthylamine	1

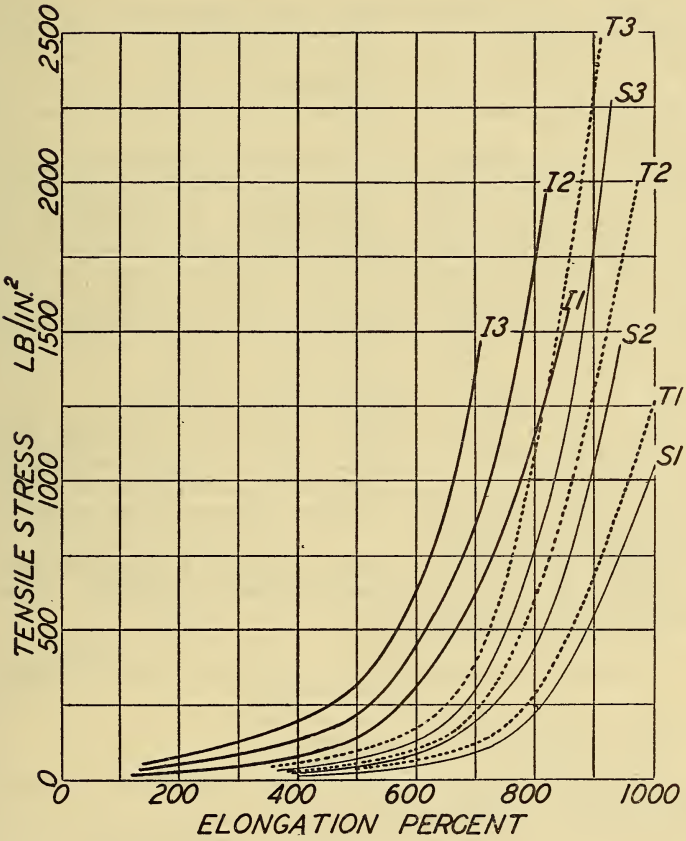

FIGURE 1.—*Stress-strain curves of soluble (S), insoluble (I), and total (T) rubbers.* Numerals 1, 2, and 3 indicate short, medium, and long cures, respectively.

Three lots were prepared, one containing the soluble fraction, the second the insoluble or gel fraction, and the third for comparison contained total rubber hydrocarbon. The total hydrocarbon was purified by the method [6] which has been described, but was not separated into fractions.

The compounds were mixed in lots of about 50 grams each by careful manipulation on a small laboratory mill. While mixing, it was quite evident that a difference existed between the two fractions. The insoluble or gel fraction as distinguished from the other rubbers was

[6] See footnote 1.

difficult to "break down" or plasticize on the mill and the resulting compound retained a gristle-like character. Compounds were vulcanized in sheets 2 by 4 inches and about 0.040 inch thick, from which dumbbell specimens were cut out for test purposes. Three periods of vulcanization were used; these were 50, 70, and 100 minutes, respectively, at 142° C. Stress-strain results obtained with each compound are shown in figure 1.

At each period of vulcanization the compound containing the soluble fraction is more extensible than that containing the insoluble, and the total hydrocarbon has an intermediate position. As the total hydrocarbon consists of 75 percent soluble and 25 percent insoluble rubber, the stress-strain curves of the compounds made with total rubber are closer to those containing the soluble fractions than to those containing the insoluble fractions. The stress-strain behavior of the total rubber is therefore in accord with the relative proportions of the two fractions present in it.

Samples of each fraction and of the total rubber hydrocarbon were pressed into thin sheets and vulcanized at room temperature by the Peachey [7] process, in which vulcanization is effected by nascent sulphur obtained by the interaction of hydrogen sulphide and sulphur dioxide. As might be expected from previous experience, it was difficult to obtain satisfactory sheets of the insoluble (gel) rubber because of its gristle-like character in the unvulcanized condition. However, some fairly uniform sheets were obtained. The sheets were vulcanized simultaneously and contained approximately 0.4 percent (see table 1) of combined sulphur, which represents a light cure. Stress-strain data of ring specimens exhibited a behavior similar to that shown in the graph. The gel rubber was the less extensible fraction, the sol rubber was the more extensible, and the curve representing the total rubber occupied a position intermediate between those representing the fractions.

The amount of combined sulphur was found by analysis in samples of all compounds used in determining stress-strain data. The results obtained are given in table 1.

TABLE 1.—*Results of the determination of "combined" sulphur in samples of the vulcanized rubbers*

Percentage of S in the vulcanized rubbers prepared from—			Conditions of curing		Accelerators used in vulcanizing
Soluble rubber hydrocarbon	Insoluble rubber hydrocarbon	Total rubber hydrocarbon	Temperature	Time	
			° C	Min.	
1.94	1.84	1.96	126	30	Tetramethylthiuram disulphide.
1.35	1.34	1.21	142	50	Triphenylguanidine.
1.57	1.64	1.45	142	70	
1.91	2.04	1.81	142	100	
0.33	0.47	0.35	----------	--------	Vulcanized by Peachey process.

From these it appears that differences in the stress-strain behavior of the fractions and the total rubber were not caused by varying amounts of combined sulphur, but must have been due to differences in the rubber, which persisted through vulcanization.

WASHINGTON, August 21, 1934.

[7] Ind. Rubber J. 63, 427 (1922).